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Environmental impact and potential remediation of contaminated land affected by Zn-Pb mining

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1. Introduction

From the Middle Ages until the beginning of the 20th century, extensive Zn-Pb mining and smelting was carried out in East-Belgium. By lack of waste treatment techniques and of sustainable management practices, metal-bearing slags and unprocessed waste were dumped. Besides the important amount of waste that is stored in huge mine tailings, the surroundings of the tailings are often contaminated as a consequence of the dispersal of contaminants by wind erosion, runoff or fluvial transport. In the present study, the distribution pattern, the actual and potential mobilisation and (natural) attenuation of Pb, Zn and Cd in the mine tailings of La Calamine and Angleur (East-Belgium) was investigated.

2. Methodology

In La Calamine and Angleur (East-Belgium), vertical profiles were sampled in detail within tailings consisting of respectively dredged mine tailing pond sediments and waste from the metallurgical process of Zn-production. Samples were also taken from overbank sediments along the Geul 7, 9 and 12 km downstream from the mine tailing pond of La Calamine and in the neighbourhood (300 m) of the dump site of Angleur.
Total metal concentrations, pH and grainsize were determined for all the samples and a mineralogical (petrography, XRD, SEM-EDX) investigation of tailing material from La Calamine and Angleur was carried out. Porewater extractions and the DIN 38414-S4 leaching test (extraction with water at a liquid/solid ratio of 10/1) were used to evaluate heavy metal leaching from the tailing material. pH_{stat} leaching tests and geochemical modelling of the pH-dependent leaching behaviour were performed on a selection of samples from both mine tailings. The feasibility of the addition of phosphates as a measure to reduce the release of Pb, Zn and Cd into the environment was also investigated.

3. Results and discussion

3. 1. Mineralogical and physico-chemical characterisation

At both locations, mine tailings and soils in the surrounding of the tailings were contaminated with Zn, Pb, Cd and As (Table 1). The mine tailing in La Calamine is located in a rural area with a low population density. The nearby Geul river flows through the mine tailing, resulting in a severe contamination of alluvial soils downstream from the tailing. The area around the mine tailing in Angleur has been urbanised.
The main minerals in the **La Calamine** mine tailing were sfalerite (ZnS), smithsonite ($ZnCO_3$), anglesite ($PbSO_4$), cerrusite ($PbCO_3$), galena (PbS), pyrite (FeS_2) and marcasite (FeS_2). Whereas more acid pH values (between 3 and 4.9) were encountered in the deeper part of the tailing (between 2.6 and 4 m depth), a lower mobility of Zn, Pb and Cd was found compared to the upper part of the tailing, where pH was in the range 5-7. The oxidation of sulphide minerals within the mine tailing releases H^+, SO_4^{2-}, Fe^{2+}, and trace metals into the porewater. Subsequent pH-buffering in carbonate-rich layers results in the precipitation of secondary minerals such as $ZnCO_3$, $FeCO_3$ and $CaSO_4.2H_2O$. These precipitation processes result in the formation of cemented layers, which show an enrichment in Cd and Zn. Whereas the carbonate-rich layers provide some natural attenuation of contaminants, elevated Zn-, Pb- and Cd concentrations are found in the porewater in the surface layers of the tailing (0-2.6 m depth).
In the mine tailing of **Angleur,** XRD analysis revealed the presence of several oxides and silicates such as franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), wollastonite ($CaSiO_3$), and traces of sulphates, sulphides and

carbonates. pH was neutral to slightly alkaline for al the samples investigated. The upper part of the tailing (0-0.7 m depth) was less contaminated than the lower part (0.7- 4 m depth). Contrary to the tailing material in La Calamine and despite the elevated total heavy metal and arsenic concentrations on the site, the DIN 38414-S4 leaching test indicates that heavy metal release is very limited and far below European limit values for slag material on dumps (category 1).

Table 1: Total Pb-, Zn-, Cd- and As-concentrations in the mine tailings and the surrounding of the mine tailings of La Calamine and Angleur. Zn and Pb in g/kg, Cd and As in mg/kg; n = number of samples

La Calamine	mine tailing (n = 20)				alluvial soils downstream (n = 100)			
	Zn	Pb	Cd	As	Zn	Pb	Cd	As
average	38	19	146	679	3.9	1.3	7	23
stdv	36	13	138	444	3.4	1.7	8	25
min	1	2.4	3	31	0.3	0.04	0.1	4
max	108	40	307	2294	13	6.5	37	121
Angleur	mine tailing (n = 91)				surrounding of the tailing (n = 16)			
	Zn	Pb	Cd	As	Zn	Pb	Cd	As
average	52	8	100	231	1.6	0.6	30	266
stdv	30	6	74	159	1.4	0.5	20	280
min	12	1.0	3	18	0.2	0.4	4	32
max	162	31	403	1928	4.5	2.3	68	942

3.2. pH-dependent leaching behaviour and potential remediation

A multidisciplinary approach, combining pH_{stat} leaching tests, solid-phase characterization (XRD, SEM-EDX) and thermodynamical modelling (MINTEQA2) confirmed that the solubility of Zn, Pb and Cd in the mine pond tailing of La Calamine is mainly controlled by Pb-Zn minerals**.** In Angleur, vitreous phases seem very important in controlling heavy metal mobility since metals that are locked up in a silicate matrix are protected against leaching.

Liming will not be an effective remediation option for the tailing in Angleur, since As and Pb will be mobilised when pH increases (Fig. 1). However, for the La Calamine dredged mine tailing pond sediments, a pH-increase significantly decreases the leachability of Zn, Cd and Pb, whereas the solubility of As is not affected and remains very low. The addition of phosphates in combination with liming results in an additional decrease of heavy metal solubility and contributes to a reduction of the release of Pb, Zn and Cd into the environment.

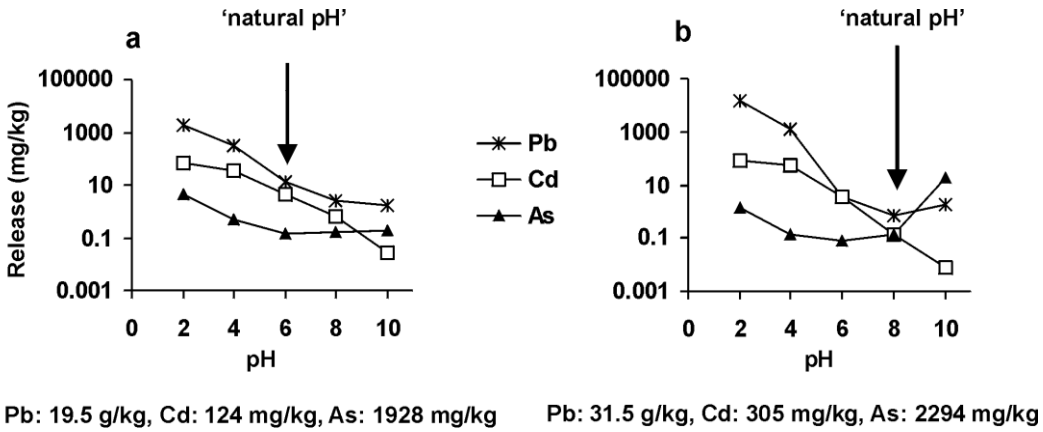

Fig. 1: pH-dependent leaching behaviuor of Pb, Cd and As in a sample from the tailing of La Calamine (a) and Angleur (b). Total Pb-, Cd- and As-concentrations and pH of the samples are also indicated.

4. Conclusion

In La Calamine, liming and the addition of phosphates can effectively reduce heavy metal leaching from the tailing. However, at both locations, wind erosion and runoff can cause the spreading of fine-grained dust, especially since the waste material is not covered. For a sustainable development of the mining areas of La Calamine and Angleur surface stabilisation is also necessary.